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14. ABSTRACT
The objective of this research was the development of the nuclear-electronic orbital approach for the investigation of hydrogen bonding and hydrogen transfer systems of interest to the Air Force. In this approach, specified hydrogen nuclei are treated quantum mechanically on the same level as the electrons with molecular orbital techniques. Recent advances within this framework significantly enhance the accuracy and applicability of this approach for the calculation of structures, energies, frequencies, vibronic couplings, and tunneling splittings. This approach was used to examine proton-coupled electron transfer reactions, which are relevant to hydrogen production and fuel cells. Furthermore, this approach was extended to positron systems and used to calculate energies and annihilation rates for small positronic-electronic molecules. Calculations were also performed on hydrogen-bonded clusters relevant to ionic liquids, which are important for the development of highly energetic and environmentally benign propellants.

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I. Introduction

The objective of this research was the development of the nuclear-electronic orbital (NEO) approach for the investigation of hydrogen bonding and hydrogen transfer systems of interest to the Air Force. In this approach, specified hydrogen nuclei are treated quantum mechanically on the same level as the electrons with molecular orbital techniques. Over the past grant period, we have focused on four main projects. The first project was the development of explicitly correlated and density functional theory approaches for incorporating electron-proton correlation effects within the NEO framework.[1-5] The second project was the development of methodology for calculating vibronic couplings and tunneling splittings in proton-coupled electron transfer and hydrogen transfer reactions.[6-8] The third project was the extension of the NEO method to calculate annihilation rates for positronic systems.[9,10] The fourth project was the study of nuclear quantum effects and anharmonic effects in hydrogen-bonded clusters, including ammonium nitrate and hydroxylammonium nitrate clusters that are relevant to ionic liquids.[11,12] Our accomplishments on these four projects are summarized below.

II. Overview of Accomplishments

II.A. Nuclear-Electronic Orbital (NEO) Method Development

In the nuclear-electronic orbital (NEO) approach,[1-5,13-19] specified nuclei are treated quantum mechanically on the same level as the electrons by solving a mixed nuclear-electronic Schrödinger equation. In previous grant cycles, we implemented the NEO approach at the Hartree-Fock (NEO-HF),[13] configuration interaction (NEO-CI),[13] multiconfigurational self-consistent-field (NEO-MCSCF),[13] and second order perturbation theory (NEO-MP2)[17] levels. Related methods have been developed by other groups.[20-29] We have shown that these methods do not include sufficient electron-proton correlation to obtain even qualitatively accurate results for certain types of systems.[14,15,19,30,31] Over the past grant period, we developed the explicitly correlated Hartree-Fock (NEO-XCHF) approach,[1,2,19] which incorporates electron-proton correlation directly into the self-consistent-field procedure for optimizing the nuclear-electronic wavefunction using Gaussian-type geminal functions. Related methods have been developed for systems in which all nuclei and electrons are treated quantum mechanically with both electron-

electron and electron-proton explicit correlation,[32] but these methods are computationally expensive and are restricted to small systems. We also designed an electron-proton functional to include electron-proton correlation within the framework of multicomponent DFT.[4]

II.A.1. NEO-XCHF

The NEO-XCHF approach is based on the following ansatz for the nuclear-electronic wavefunction:[1,19]

$$\Psi_{gem} = \Phi^e \Phi^p \left[1 + \sum_{i=1}^{N_e} \sum_{i'=1}^{N_p} \sum_{k=1}^{N_{gem}} b_k \exp\left[-\gamma_k \left| \mathbf{r}_i^e - \mathbf{r}_{i'}^p \right|^2 \right] \right], \tag{1}$$

where N_e, N_p, and N_{gem} denote the numbers of electrons, quantum protons, and geminal functions, Φ^e and Φ^p are electronic and nuclear Slater determinants comprised of molecular orbitals, $\mathbf{r}_i^e$ and $\mathbf{r}_{i'}^p$ denote electronic and nuclear coordinates, and b_k and γ_k are geminal parameters that are pre-determined from model systems. Based on this ansatz, the variational method is used to minimize the total energy with respect to the electronic and nuclear molecular orbitals. The resulting electronic and nuclear Hartree-Fock-Roothaan equations are solved iteratively until self-consistency. In this manner, the explicit electron-proton correlation is incorporated directly into the self-consistent-field procedure for optimizing the nuclear-electronic wavefunction. Note that previously explicit electron-electron correlation[33-36] was included in MP2 corrections for electronic structure calculations,[37-57] but such an approach is not suitable for electron-proton correlation because the Hartree-Fock reference is inadequate.

Over the past grant period, we derived the general expressions for the total energy and the electronic and nuclear Fock operators corresponding to Eq. (1) in a spin orbital basis for many-electron systems.[1] We also derived the restricted Hartree-Fock (RHF) formulation of NEO-XCHF for closed-shell electronic systems in an atomic orbital basis. In addition, we performed benchmark calculations on the [He-H-He]$^+$ model system and compared the NEO-XCHF method to the NEO-HF and grid-based methods. Recently we identified a technical problem with the computer code and are working on correcting the problem and generating new values for these benchmarking calculations. Since the NEO-XCHF method includes the significant electron-proton correlation, it will provide an accurate description of the proton density and the physical properties relying on this density.

Subsequently, we extended the NEO-XCHF approach to treat many-electron, many-proton systems and to describe a broader class of systems that require a more general form of the wavefunction (i.e., open-shell and multireference wavefunctions).[2] This general formulation of the NEO-XCHF approach is based on a density matrix representation. We derived expressions for the one- and two-particle geminal densities, as well as the total energy, in terms of auxiliary densities corresponding to the molecular orbitals in the Slater determinants. We also derived expressions for the total energy and the electronic and nuclear Fock matrices in an atomic orbital basis for the special case of single determinant electronic and nuclear wavefunctions and closed-shell electronic systems. These expressions can be substituted directly into the standard Hartree-Fock-Roothaan equations, which are solved iteratively to self-consistency. The density matrix representation facilitates the development of approximate NEO-XCHF methods, in which specified high-order density terms are neglected to decrease the computational expense, and provides the foundation for the development of electron-proton functionals within the framework of multicomponent DFT. Note that an alternative approach has also been used to extend the density matrix methods[58-60] to multicomponent systems recently.[61-63]

II.A.2. Multicomponent DFT

In multicomponent DFT, both electrons and nuclei are treated quantum mechanically within the DFT framework.[28,29,64,65] Although the existence of ground state density functionals in terms of the one-particle electronic and nuclear densities has been proven,[64,66] the development of such electronic-nuclear functionals is challenging. Reparametrizing existing electronic functionals for use as electron-proton functionals[67,68] is not physically meaningful due to the fundamental differences between electron-electron and electron-proton interactions. Approximate electronic-nuclear functionals in terms of the one-particle electron density and the N_n-particle nuclear density matrix have been proposed for systems in which all N_n nuclei are treated quantum mechanically, but this approach has not been extended beyond H_2.[28,29]

Over the past grant period, we developed and implemented a strategy for the design of electron-proton density functionals in multicomponent DFT.[4] According to the Hohenberg-Kohn theorem for multicomponent systems, the total energy is a functional of the one-particle electronic and nuclear densities, ρ^e and ρ^p. Within the Kohn-Sham formalism, the total energy can be expressed as follows:

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$$E\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]=\int V_{\mathrm{eC}}\rho^{\mathrm{e}}d\mathbf{r}^{\mathrm{e}}+\int V_{\mathrm{pC}}\rho^{\mathrm{p}}d\mathbf{r}^{\mathrm{p}}+E_{\mathrm{ref}}\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]$$
$$+E_{\mathrm{xc}}^{\mathrm{e}}\left[\rho^{\mathrm{e}}\right]+E_{\mathrm{xc}}^{\mathrm{p}}\left[\rho^{\mathrm{p}}\right]+E_{\mathrm{epc}}\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right] \tag{2}$$

On the right side of this expression, the first two terms correspond to the interaction of the electrons and quantum protons with the classical nuclei, and the third term is defined to include the kinetic energies of the electrons and quantum protons for non-interacting particles and the so-called "classical" Coulomb interactions for all quantum particles (i.e., electron-electron, electron-proton, and proton-proton). The term $E_{\mathrm{xc}}^{\mathrm{e}}\left[\rho^{\mathrm{e}}\right]$ is the exchange-correlation functional for the electrons and could be chosen to be an existing electronic functional. The term $E_{\mathrm{xc}}^{\mathrm{p}}\left[\rho^{\mathrm{p}}\right]$ is the exchange-correlation functional for the quantum protons and is typically negligible because the proton densities are localized and spatially separated in molecular systems. In practice, each quantum proton occupies a different spatial orbital, and Hartree-Fock exchange for protons is included to alleviate potential difficulties with self-interaction. The last term, $E_{\mathrm{epc}}\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]$, is the electron-proton correlation functional that was the focus of our studies. Within the Kohn-Sham framework, the one-particle electronic and nuclear densities are represented in terms of Kohn-Sham orbitals, and the variational method is used to obtain analogs of the electronic and nuclear Hartree-Fock-Roothaan equations, which are solved iteratively to self-consistency.

In our studies, we defined the general electron-proton functional as

$$E_{\mathrm{epc}}\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]=\int\int d\mathbf{r}^{\mathrm{e}}d\mathbf{r}^{\mathrm{p}}r_{\mathrm{ep}}^{-1}\rho^{\mathrm{ep}}(\mathbf{r}^{\mathrm{e}},\mathbf{r}^{\mathrm{p}})-\int\int d\mathbf{r}^{\mathrm{e}}d\mathbf{r}^{\mathrm{p}}r_{\mathrm{ep}}^{-1}\rho^{\mathrm{e}}(\mathbf{r}^{\mathrm{e}})\rho^{\mathrm{p}}(\mathbf{r}^{\mathrm{p}}), \tag{3}$$

which is the difference between the "exact" electron-proton interaction based on the electron-proton pair density ρ^{ep} and the "classical" electron-proton Coulomb interaction based on the one-particle densities. We then used the explicitly correlated geminal wavefunction ansatz in Eq. (1) to obtain an approximate expression for the electron-proton pair density in terms of the one-particle electron and proton densities (i.e., $\rho^{\mathrm{ep}} \approx F\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]$). Substitution of this expression $F\left[\rho^{\mathrm{e}},\rho^{\mathrm{p}}\right]$ for ρ^{ep} into Eq. (3) provided an electron-proton functional in terms of one-particle densities.[4] The application of this NEO-DFT method to the [He-H-He]$^{+}$ model system will be re-examined with the new version of the code. In addition to the development of this specific functional, we derived a number of important mathematical properties of the exact universal multicomponent density functional.[5]

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We also developed the NEO-DFT(ee) method for including electron-electron correlation within the NEO framework.[3] In the initial implementation of the NEO-DFT(ee) approach, the electron-proton correlation was neglected for simplicity. In the context of Eq. (2), the electronic exchange-correlation functional was chosen to be the standard B3LYP electronic functional,[69-71] the proton exchange-correlation functional was chosen to be Hartree-Fock exchange, and the electron-proton correlation functional was neglected. This approach includes feedback between the correlated electron density and the nuclear wavefunction. We applied this approach to bihalides, and the NEO-DFT(ee) optimized bihalide structures are in excellent agreement with the vibrationally averaged geometries from grid-based quantum dynamical methods.
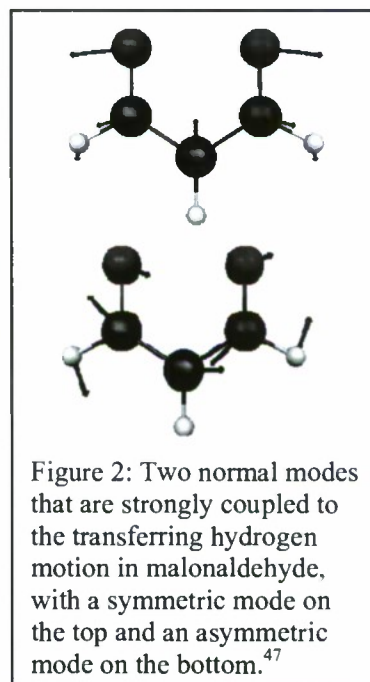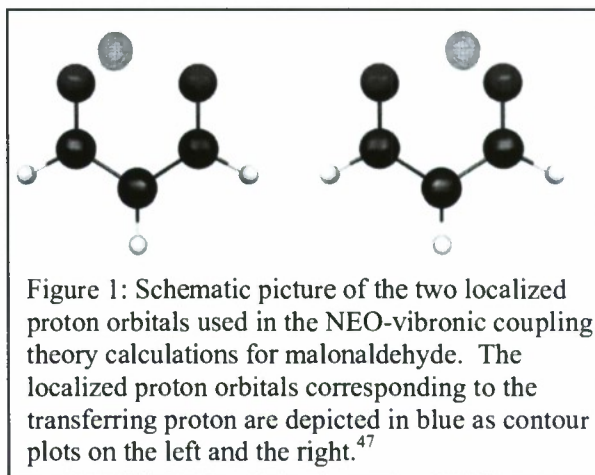
II.B. Vibronic Couplings and Tunneling Splittings

We developed methodology for calculating vibronic couplings for proton-coupled electron transfer (PCET) reactions.[6,8,72] In this methodology, all electrons and the transferring hydrogen nucleus are treated quantum mechanically, and the vibronic coupling is defined as the Hamiltonian matrix element between the reactant and product mixed electron-proton vibronic wavefunctions. We implemented a grid-based nonadiabatic method[72,73] and the NEO nonorthogonal configuration interaction method[16] for calculating vibronic couplings. We utilized this methodology to investigate the impact of substituents on the vibronic coupling for the phenoxyl/phenol self-exchange reaction,[6] which occurs by a PCET mechanism.[72,74,75] The results indicate that electron donating groups enhance the vibronic coupling, while electron withdrawing groups attenuate the vibronic coupling. Thus, if all other aspects of the reaction are the same, then electron donating groups will increase the rate, while electron withdrawing groups will decrease the rate. We also analyzed correlations between the vibronic coupling and physical properties of the phenol, such as Hammett constants, bond dissociation enthalpies, ionization potentials, redox potentials, and pK_a values.

In addition, we combined the NEO method with vibronic coupling theory to calculate hydrogen tunneling splittings in polyatomic molecules.[7] In this NEO-vibronic coupling approach, the transferring proton and all electrons are treated quantum mechanically at the NEO level, and the other nuclei are treated quantum mechanically using vibronic coupling theory.[76,77] The dynamics of the molecule are described by a vibronic Hamiltonian in an approximately diabatic basis of two localized nuclear-electronic states for the electrons and transferring proton.

This approach is computationally practical and efficient for relatively large molecules, and the accuracy can be improved systematically. An alternative approach involving multidimensional wavepacket dynamics has been used to study hydrogen bonding in other systems.[78]

We used the NEO-vibronic coupling approach to calculate the hydrogen tunneling splitting for malonaldehyde.[7] This system is ideal for benchmarking purposes because

Figure 1: Schematic picture of the two localized proton orbitals used in the NEO-vibronic coupling theory calculations for malonaldehyde. The localized proton orbitals corresponding to the transferring proton are depicted in blue as contour plots on the left and the right.[47]

numerous theoretical calculations of the ground state tunneling splitting of malonaldehyde have been published.[79-92] The two localized NEO states are depicted in Figure 1, and two of the modes strongly coupled to the hydrogen tunneling are depicted in Figure 2. The tunneling splitting of 24.5 cm^{-1} calculated with the NEO-vibronic coupling approach at the MP2 level of electronic structure theory is in excellent agreement with the experimental value of 21.6 cm^{-1}.

This approach also enables the identification of the dominant modes coupled to the transferring hydrogen motion and provides insight into their roles in the hydrogen tunneling process. The NEO-vibronic coupling approach is not as accurate as methods such as multiconfigurational time-dependent Hartree[89,93] and diffusion Monte Carlo,[91,92] but it is designed to provide qualitatively accurate tunneling splittings at lower computational cost, thereby enabling calculations on larger molecules that cannot be studied with the more expensive methods. In addition, this approach is capable of including nonadiabatic effects between the electrons and the proton and can be used to identify the dominant modes that should be included in reduced-dimensionality calculations with more accurate methods.

Figure 2: Two normal modes that are strongly coupled to the transferring hydrogen motion in malonaldehyde, with a symmetric mode on the top and an asymmetric mode on the bottom.[47]

II.C. Positrons

We modified and extended the NEO methods to study mixed electron-positron quantum systems.[9,10] In this approach, all electrons and the positron are treated quantum mechanically, while the nuclei are represented as classical point charges. The initial work was performed in collaboration with Paul Adamson and Larry Burggraf at the Air Force Institute of Technology at Wright-Patterson Air Force Base.[9] Dr. Adamson, who was a graduate student with Dr. Burggraf at the time, implemented the NEO-HF, NEO-MP2, and NEO-FCI methods to calculate electron-positron annihilation rates. He applied these methods to positronium hydride (PsH), which consists of a proton, two electrons, and a positron, and to the e^{+}LiH molecule. Even NEO-FCI, which is computationally impractical for larger systems, produced an annihilation rate that was less than 40% of the most accurate results for PsH.[9] Successful calculations of positron annihilation rates in small systems such as PsH have relied on an explicit treatment of dynamical correlation.[94,95] While such methods typically produce highly accurate annihilation rates, they are computationally expensive and are not easily extended to systems with more than a few electrons.

Recently we extended the NEO-XCHF method to electron-positron systems and calculated the positron annihilation rate for PsH.[10] The NEO-XCHF method is more computationally efficient than the explicitly correlated methods previously applied to this system because only the electron-positron dynamical correlation is treated explicitly, so fewer parameters must be optimized during the variational procedure. The annihilation rate is a measure of the local property of the wavefunction in the region of small electron-positron distances, where the electron-positron dynamical correlation is significant and is well-described by the explicitly correlated geminal wavefunction. This approach is not expected to be more accurate than many other methods that were used successfully to calculate positron annihilation rates in small positron systems,[94,95] but it is designed to be more easily extendable to larger systems. The NEO-XCHF annihilation rate for PsH is within 20% of the most accurate values available and is calculated at a fraction of the computational cost. These results suggest that qualitatively accurate positron annihilation rates can be calculated treating only electron-positron correlation explicitly, leading to significant computational savings by neglecting electron-electron dynamical correlation. Thus, the NEO-XCHF approach could potentially enable the

calculation of qualitatively accurate positron annihilation rates for larger positron systems. Given the wide range of experimentally measured positron annihilation rates,[96,97] such qualitative predictions are expected to be useful for technological applications of interest to the Air Force.

II.D. Nuclear Quantum Effects and Anharmonic Effects in Hydrogen-Bonded Clusters

We investigated the impact of nuclear quantum effects on hydrogen bonding for a series of hydrogen fluoride (HF)$_n$ clusters and a partially solvated fluoride anion, $F^-(H_2O)$. The nuclear quantum effects were included using the path integral formalism in conjunction with the Car-Parrinello molecular dynamics (PICPMD) method and using the second-order vibrational perturbation theory (VPT2) approach. For the HF clusters, we observed a directional change in the impact of nuclear quantum effects on the hydrogen bonding strength as the clusters evolve toward the condensed phase. Specifically, the inclusion of nuclear quantum effects increases the F---F distances for the (HF)$_{n=2-4}$ clusters and decreases the F---F distances for the (HF)$_{n>4}$ clusters. This directional change occurs because the enhanced electrostatic interactions between the HF monomers become more dominant than the zero point energy effects of librational modes as the size of the HF clusters increases. For the $F^-(H_2O)$ system, the inclusion of nuclear quantum effects decreases the F---O distance and strengthens the hydrogen bonding interaction between the fluoride anion and the water molecule because of enhanced electrostatic interactions. The vibrationally averaged ^{19}F shielding constant for $F^-(H_2O)$ we found to be significantly lower than the value for the equilibrium geometry, indicating that the electronic density on the fluorine decreases as a result of the quantum delocalization of the shared hydrogen. Deuteration of this system leads to an increase in the vibrationally averaged F---O distance and nuclear magnetic shielding constant because of the smaller degree of quantum delocalization for deuterium.

We also investigated hydrogen-bonded clusters that are relevant to ionic liquids, which are promising candidates for highly energetic and environmentally benign propellants. In this study, we characterized the covalent and ionic clusters of ammonium nitrate and hydroxyl ammonium nitrate using density functional theory and second-order vibrational perturbation theory.[15] The most stable structures are covalent acid-base pairs for the monomers and ionic acid-base pairs for the dimers. The hydrogen bonding distances are greater in the ionic dimers than in the covalent monomers, and the stretching frequencies are significantly different in the

covalent and ionic clusters. The anharmonicity of the potential energy surfaces is found to influence the geometries, frequencies, and nuclear magnetic shielding constants for these systems. The inclusion of anharmonic effects significantly decreases many of the calculated vibrational frequencies in these clusters and improves the agreement of the calculated frequencies with the experimental data available for the isolated neutral species. The calculations of nuclear magnetic shielding constants for all nuclei in these clusters illustrate that quantitatively accurate predictions of nuclear magnetic shieldings for comparison to experimental data require the inclusion of anharmonic effects. These calculations of geometries, frequencies, and shielding constants provide insight into the significance of anharmonic effects in ionic materials and provide data that will be useful for the parameterization of molecular mechanical forcefields for ionic liquids. Anharmonic effects will be particularly important for the study of proton transfer reactions in ionic materials.

III. Summary

To summarize, we have developed the nuclear-electronic orbital (NEO) approach for incorporating nuclear quantum effects into electronic structure calculations. This approach enables the calculation of structures, energies, frequencies, tunneling splittings, and vibronic couplings for hydrogen bonding and hydrogen transfer systems. The advances and extensions developed over the past grant period have enhanced the accuracy and applicability of this approach. Two particularly promising directions are the inclusion of explicit electron-proton correlation in wavefunction methods and the design of electron-proton functionals in multicomponent density functional theory. In addition to this method development, we have performed calculations of vibronic couplings for proton-coupled electron transfer systems and hydrogen tunneling splittings for molecular systems such as malonaldehyde. Furthermore, applications of quantum dynamical methods to covalent and ionic clusters have provided insights into the hydrogen bonding properties of systems related to ionic liquids. These types of calculations provide information that should aid in the design and characterization of highly energetic materials of interest to the Air Force.

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Personnel Supported

Benjamin Auer (postdoc)
Arindam Chakraborty (postdoc)
Dhruva Chakravorty (graduate student)
Laura Fernandez (graduate student)
Anirban Hazra (postdoc)
Malika Kumarasiri (graduate student)
Michael Pak (postdoc)
Jonathan Skone (graduate student)
Chet Swalina (graduate student)

Publications during funding period (asterisks indicate work supported by AFOSR)

1. S. Hammes-Schiffer, "Proton-coupled electron transfer reactions: Theoretical formulation and applications," pp. 479-502 in *Handbook of Hydrogen Transfer. Volume 2: Physical and Chemical Aspects of Hydrogen Transfer*, eds. J. T. Hynes, J. P. Klinman, H.-H. Limbach and R. L. Schowen (Wiley-VCH, Weinheim, 2007).

2. S. J. Benkovic and S. Hammes-Schiffer, "Dihydrofolate reductase: Hydrogen tunneling and protein motion," pp. 1439-1454 in *Handbook of Hydrogen Transfer. Volume 4: Biological Aspects of Hydrogen Transfer*, eds. J. T. Hynes, J. P. Klinman, H.-H. Limbach and R. L. Schowen (Wiley-VCH, Weinheim, 2007).

3. E. Hatcher, A. V. Soudackov, and S. Hammes-Schiffer, "Proton-coupled electron transfer in soybean lipoxygenase: Dynamical behavior and temperature dependence of kinetic isotope effects," *J. Am. Chem. Soc.* **129**, 187-196 (2007).

4. * M. Kumarasiri, C. Swalina, and S. Hammes-Schiffer, "Anharmonic effects in ammonium nitrate and hydroxylammonium nitrate clusters," *J. Phys. Chem. B* **111**, 4653-4658 (2007).

5. * C. Swalina, Q. Wang, A. Chakraborty, and S. Hammes-Schiffer, "Analysis of nuclear quantum effects on hydrogen bonding," *J. Phys. Chem. A* **111**, 2206-2212 (2007).

6. * M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, "Density functional theory treatment of electron correlation in the nuclear-electronic orbital approach," *J. Phys. Chem. A* **111**, 4522-4526 (2007).

7. H. Ishikita, A. V. Soudackov, and S. Hammes-Schiffer, "Buffer-assisted proton-coupled electron transfer in a model rhenium-tyrosine complex," *J. Am. Chem. Soc.* **129**, 11146-11152 (2007).

8. * M. K. Ludlow, J. H. Skone, and S. Hammes-Schiffer, "Substituent effects on the vibronic coupling for the phenoxyl/phenol self-exchange reaction," *J. Phys. Chem. B* **112**, 336-343 (2008).

9. S. Hammes-Schiffer, E. Hatcher, H. Ishikita, J. H. Skone, and A. V. Soudackov, "Theoretical studies of proton-coupled electron transfer: Models and concepts relevant to bioenergetics," *Coordination Chemistry Reviews* **252**, 384-394 (2008).

10. * P. E. Adamson, X. F. Duan, L. W. Burggraf, M. V. Pak, C. Swalina, and S. Hammes-Schiffer, "Modeling positrons in molecular electronic structure calculations with the nuclear-electronic orbital method," *J. Phys. Chem. A* **112**, 1346-1351 (2008).

11. S. J. Benkovic, G. G. Hammes, and S. Hammes-Schiffer, "Free energy landscape of enzyme catalysis," *Biochemistry* **47**, 3317-3321 (2008).

12. C. Venkataraman, A. V. Soudackov, and S. Hammes-Schiffer, "Theoretical formulation of nonadiabatic electrochemical proton-coupled electron transfer at metal-solution interfaces," *J. Phys. Chem. C* **112**, 12386-12397 (2008).

13. * A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, "Inclusion of explicit electron-proton correlation in the nuclear-electronic orbital approach using Gaussian-type geminal functions," *J. Chem. Phys.* **129**, 014101 (2008).

14. I. Navrotskaya, A. V. Soudackov, and S. Hammes-Schiffer, "Model system-bath Hamiltonian and nonadiabatic rate constants for proton-coupled electron transfer at electrode-solution interfaces," *J. Chem. Phys.* **128**, 244712 (2008).

15. * A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, "Development of electron-proton density functionals for multicomponent density functional theory," *Phys. Rev. Lett.* **101**, 153001 (2008).

16. * S. Hammes-Schiffer and A. V. Soudackov, "Proton-coupled electron transfer in solution, proteins, and electrochemistry," *J. Phys. Chem. B* **112**, 14108-14123 (2008) (Centennial Feature Article).

17. D. K. Chakravorty, M. Kumarasiri, A. V. Soudackov, and S. Hammes-Schiffer, "Implementation of umbrella integration within the framework of the empirical valence bond approach," *J. Chem. Theory and Comp.* **4**, 1974-1980 (2008).

18. * A. Chakraborty and S. Hammes-Schiffer, "Density matrix formulation of the nuclear-electronic orbital approach with explicit electron-proton correlation," *J. Chem. Phys.* **129**, 204101 (2008).

19. S. Hammes-Schiffer, "Selected Theoretical Models and Computational Methods for Enzymatic Tunnelling," pp. 79-104 in *Quantum Tunnelling in Enzyme-Catalysed Reactions*, eds. R. K. Allemann and N. S. Scrutton (Royal Society of Chemistry, Cambridge, 2009).

20. S. J. Edwards, A. V. Soudackov, and S. Hammes-Schiffer, "Analysis of kinetic isotope effects for proton-coupled electron transfer reactions," *J. Phys. Chem. A* **113**, 2117-2126 (2009).

21. * A. Hazra, J. H. Skone, and S. Hammes-Schiffer, "Combining the nuclear-electronic orbital approach with vibronic coupling theory: Calculation of the tunneling splitting for malonaldehyde," *J. Chem. Phys.* **130**, 054108 (2009).

22. * M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, "Calculation of the positron annihilation rate in PsH with the positronic extension of the explicitly correlated nuclear-electronic orbital method," *J. Phys. Chem. A* **113**, 4004-4008 (2009).

23. M. Kumarasiri, G. A. Baker, A. V. Soudackov, and S. Hammes-Schiffer, "Computational approach for ranking mutant enzymes according to catalytic reaction rates," *J. Phys. Chem. B* **113**, 3579-3583 (2009).

24. M. K. Ludlow, A. V. Soudackov, and S. Hammes-Schiffer, "Theoretical analysis of the unusual temperature dependence of the kinetic isotope effect in quinol oxidation," *J. Am. Chem. Soc.* **131**, 7094-7102 (2009).

25. I. Navrotskaya and S. Hammes-Schiffer, "Electrochemical proton-coupled electron transfer: Beyond the golden rule," *J. Chem. Phys.* **131**, 024112 (2009).

26. S. Hammes-Schiffer, "Theory of proton-coupled electron transfer in energy conversion processes," *Acc. Chem. Res.* **42**, 1881-1889 (2009).

27. L. Hammarström and S. Hammes-Schiffer, "Artificial photosynthesis and solar fuels: Guest editorial," *Acc. Chem. Res.* **42**, 1859-1860 (2009).

28. * A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, "Properties of the exact universal functional in multicomponent density functional theory," *J. Chem. Phys.* **131**, 124115 (2009).

29. C. Venkataraman, A. V. Soudackov, and S. Hammes-Schiffer, "Photoinduced homogeneous proton-coupled electron transfer: Model study of isotope effects on reaction dynamics," *J. Chem. Phys.* **131**, 154502 (2009).

30. S. J. Edwards, A. V. Soudackov, and S. Hammes-Schiffer, "Driving force dependence of rates for nonadiabatic proton and proton-coupled electron transfer: Conditions for inverted region behavior," *J. Phys. Chem. B* **113**, 14545-14548 (2009).

31. D. K. Charavorty, A. V. Soudackov, and S. Hammes-Schiffer, "Hybrid quantum/classical molecular dynamics simulations of the proton transfer reactions catalyzed by ketosteroid isomerase: Analysis of hydrogen bonding, conformational motions, and electrostatics," *Biochemistry* **48**, 10608-10619 (2009).

Interactions/Transitions during funding period

a. Presentations during funding period

1. California Institute of Technology, Pasadena, California, November 28, 2006 (invited seminar): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

2. Berkeley Mini Stat Mech Meeting, Berkeley, California, January 12-14, 2007 (invited talk): "Proton-Coupled Electron Transfer Reactions: Dynamics and Kinetic Isotope Effects"

3. Gordon Research Conference on Electrochemistry, Ventura, California, January 14-19, 2007 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution and Proteins"

4. DARPA Control of Protein Conformations Kickoff Meeting, San Francisco, California, February 1-2, 2007 (invited talk): "Elucidation of Allosteric Mechanisms with Molecular Dynamics"

5. Gordon Research Conference on Gaseous Ions: Structures, Energetics and Reactions, Ventura, California, February 25-March 2, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Calculation of Structures, Frequencies, and Couplings"

6. American Chemical Society National Meeting, Symposium entitled Measures of Accuracy and Reliability in Molecular Simulation, Chicago, Illinois, March 25-29, 2007 (invited talk): "Hybrid Quantum-Classical Molecular Dynamics of Hydrogen Transfer Reactions in Enzymes"

7. Annual Meeting of the American Society for Biochemistry and Molecular Biology, Symposium entitled Computational Studies of Mechanistic and Dynamical Aspects of Enzyme Reactions, Washington, DC, April 28-May 2, 2007 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

8. 7th Annual Symposium of the Centre for Research in Molecular Modeling (CERMM), Montreal, Canada, May 4-6, 2007 (plenary lecture): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

9. AFOSR Contractor's Conference, Irvine, California, May 20-22, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Recent Advances and Applications"

10. Molecular Quantum Mechanics International Conference, Budapest, Hungary, May 29-June 3, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

11. Gordon Research Conference on Molecular and Cellular Bioenergetics, Andover, New Hampshire, June 17-22, 2007 (invited talk): "Proton-Coupled Electron Transfer in Proteins: Dynamics and Kinetic Isotope Effects"

12. Midwest Theoretical Chemistry Conference, Bloomington, Indiana, June 28-30, 2007 (plenary talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

13. CECAM workshop on Theoretical and Experimental Exploration of Quantum Dynamics in Condensed Phase Chemical Systems, Dublin, Ireland, August 7-10, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

14. American Chemical Society National Meeting, Symposium entitled Hydration: From Clusters to Solution, Boston, Massachusetts, August 19-23, 2007 (invited talk): "Role of Water in Proton-Coupled Electron Transfer Reactions"

15. American Chemical Society National Meeting, Symposium entitled Strategies in Enzymatic Oxidation Catalysis, Boston, Massachusetts, August 19-23, 2007 (invited talk): "Proton-Coupled Electron Transfer in Soybean Lipoxygenase: Dynamical Behavior and Kinetic Isotope Effects"

16. Pittsburgh University, Pittsburgh, Pennsylvania, September 20, 2007 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

17. XIV International Workshop on Quantum Atomic and Molecular Tunneling in Solids and other Condensed Phases, Houston, Texas, October 28-November 1, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

18. 16th Conference on Current Trends in Computational Chemistry, Jackson, Mississippi, November 2-3, 2007 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

19. Gordon Research Conference in Biomolecular Interactions and Methods, Ventura, California, January 13-18, 2008 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

20. Wayne State University, Detroit, Michigan, March 18, 2008 (invited talk, medical school): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

21. Wayne State University, Detroit, Michigan, March 19, 2008 (invited talk, physical chemistry seminar): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

22. University of California Berkeley Structural and Quantitative Biology seminar, April 21, 2008 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

23. Conference on Protein Dynamics and Catalysis, Tarrytown, New York, May 2-4, 2008 (invited talk): "Proton-Coupled Electron Transfer in Soybean Lipoxygenase: Dynamical Behavior and Kinetic Isotope Effects"

24. Central East Regional ACS Meeting, Symposium entitled Theoretical Models of Solvation: Methods and Applications, Columbus, Ohio, June 11-14, 2008 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution and at Electrochemical Interfaces"

25. 13th International Workshop on Quantum Systems in Chemistry and Physics (QSCP-XIII), Lansing, Michigan, July 6-12, 2008 (invited talk): "Nuclear-Electronic Orbital Approach: Including Nuclear Quantum Effects in Electronic Structure Calculations"

26. 6th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VI), Vancouver, Canada, July 19-24, 2008 (plenary talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

27. 6th Congress of the International Society for Theoretical Chemical Physics (ISTCP-VI), Vancouver, Canada, July 19-24, 2008 (invited talk): "Hybrid Quantum/Classical Molecular Dynamics of Hydrogen Transfer Reactions in Enzymes"

28. Gordon Research Conference on Electron Donor Acceptor Interactions, Newport, Rhode Island, August 3-8, 2008 (invited talk): "Proton-Coupled Electron Transfer Reactions in Solution, Proteins, and Electrochemistry"

29. American Chemical Society National Meeting, Symposium entitled Water Mediated Interactions, Philadelphia, Pennsylvania, August 17-21, 2008 (talk): "Role of Water in Proton-Coupled Electron Transfer"

30. American Chemical Society National Meeting, Symposium entitled Biological and Biomimetic Interfacial Electron Transfer, Philadelphia, Pennsylvania, August 17-21, 2008 (invited talk): "Electrochemical Proton-Coupled Electron Transfer"

31. University of Akron, Akron, Ohio, November 11, 2008 (invited talk): "Proton-Coupled Electron Transfer in Solution, Proteins, and Electrochemistry"

32. Akron Section Award Address, Akron, Ohio, November 11, 2008 (award talk): "How do Biological Enzymes Work?"

33. Osaka University Forum 2008, San Francisco, California, December 8-11, 2008 (invited talk): "Proton-Coupled Electron Transfer in Energy Conversion"

34. Workshop on Chemical Dynamics: Challenges and Approaches for a Thematic Year in Mathematics and Chemistry at the Institute for Mathematics and its Applications at the University of Minnesota, Minneapolis, Minnesota, January 12-16, 2009 (invited talk): "Nuclear-Electronic Orbital Approach: Electron-Proton Correlation, Multicomponent Density Functional Theory, and Tunneling Splittings"

35. Gordon Research Conference on Protons and Membrane Reactions, Ventura, California, February 22-27, 2009 (invited talk): "Proton-Coupled Electron Transfer Reactions in Enzymes: Hydrogen Tunneling and Protein Motion"

36. Sanibel Symposium, St. Simons Island, Georgia, February 26- March 3, 2009 (invited talk): "Proton-Coupled Electron Transfer Reactions in Enzymes: Hydrogen Tunneling and Protein Motion"

37. American Chemical Society National Meeting, Symposium entitled Advances in Electronic Structure Theory and First Principles Dynamics, Salt Lake City, Utah, March 22-26, 2009 (invited talk): "Electron-Proton Correlation in the Nuclear-Electronic Orbital Approach: Explicit Correlation and Multicomponent Density Functional Theory"

38. American Chemical Society National Meeting, Symposium entitled Functional Motions in Enzyme Catalysis, Salt Lake City, Utah, March 22-26, 2009 (invited talk): "Proton-Coupled Electron Transfer in Soybean Lipoxygenase: Impact of Mutation on Enzyme Motions Coupled to Catalysis"

39. Ohio State University, Columbus, Ohio, April 13, 2009 (invited talk): "Hydrogen Tunneling and Protein Motion in Enzyme Reactions"

40. Franklin Institute, Philadelphia, Pennsylvania, April 23, 2009 (invited talk): "Impact of Enzyme Motion on Activity"

41. University of Washington, Seattle, Washington, April 29, 2009 (invited talk): "Proton-Coupled Electron Transfer in Solution, Proteins, and Electrochemistry"

42. AFOSR Contractor's Meeting, San Diego, California, May 17-19, 2009 (invited talk): "Nuclear-Electronic Orbital Approach: Electron-Proton Correlation and Multicomponent Density Functional Theory"

43. Gordon Research Conference on Biological Molecules in the Gas Phase and in Solution, Tilton, New Hampshire, July 5-9, 2009 (invited talk): "Proton and Hydrogen Transfer Reactions in Enzymes"

44. Canadian Computational Chemistry Conference, Halifax, Nova Scotia, Canada, July 20-24, 2009 (invited talk): "Nuclear-Electronic Orbital Approach: Electron-Proton Correlation and Multicomponent Density Functional Theory"

45. American Chemical Society National Meeting, Symposium entitled The Physical Chemistry of Photon to Fuel Conversion, Washington, D.C., August 16-20, 2009 (invited talk): "Proton-Coupled Electron Transfer in Energy Conversion"

46. Northwestern University, Evanston, Illinois, November 4, 2009 (invited talk): "Proton-Coupled Electron Transfer in Catalysis and Energy Conversion"

b. Consultative and advisory functions

None

c. Transitions

None

New discoveries, inventions, or patent disclosures

None

Honors/Awards during funding period

American Chemical Society Akron Section Award, 2008

Senior Editor for *The Journal of Physical Chemistry*, 2001 – present

Senior Editor for *The Journal of Physical Chemistry Letters*, 2009 – present

Rotation as Chair of the Physical Chemistry Division of the American Chemical Society, 2008 – 2013

Editorial Advisory Board for the *Journal of Chemical Theory and Computation*, 2010 – present

Editorial Advisory Board for *The Journal of the American Chemical Society*, 2008 – present

Editorial Advisory Board for *Accounts of Chemical Research*, 2006 – present

Member of BESAC (Basic Energy Sciences Advisory Committee) for the Department of Energy, 2008 – 2012

Guest Editor for a special issue of *Accounts of Chemical Research* on Artificial Photosynthesis and Solar Fuels, 2009

Guest Editor for a special issue of *Chemical Reviews* on Proton-Coupled Electron Transfer, 2010

Advisory Board for *Theoretical Chemistry Accounts*, 2002 – 2008

Member of a Committee of Visitors (COV) for the Chemical Sciences, Geosciences, and Biosciences Division in Basic Energy Sciences, serving on a panel that covers the research activities in the Photochemistry and Radiation Research and Condensed-phase Chemical Physics programs, April 2008

Co-organized a Workshop entitled "Chemical Dynamics: Challenges and Approaches" for a Thematic Year in Mathematics and Chemistry at the Institute for Mathematics and its Applications at the University of Minnesota, January 2009

Organized the symposium entitled "Quantum Mechanics and Statistical Mechanics: Can One Avoid the Other?" for the American Chemical Society National Meeting in August, 2007 in Boston, MA

Organized the symposium entitled "Computational Studies of Mechanistic and Dynamical Aspects of Enzyme Reactions" for the ASBMB meeting in May, 2007 in Washington D.C.